

# Environmental Radionuclide Analyses around Nuclear Installations in Northern Switzerland

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**Summary.** Beside on-line dose rate measurements, various radiochemical methods are applied at the Paul Scherrer Institute for immission measurements around nuclear facilities in Northern Switzerland. The radioanalytical procedures are carried out on soil and grass samples mainly for determination of the activity concentrations of pure anthropogenic  $\alpha$ - and  $\beta$ -emitters such as fissiogenic  $^{89}\text{Sr}$ ,  $^{90}\text{Sr}$  and isotopes of transuranium elements such as  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{244}\text{Cm}$ . In particular, for rapid determination of Pu-isotopes, a simple and fast method was developed based on anion exchange chromatography and  $\alpha$ -spectrometry. After leaching and addition of  $^{242}\text{Pu}$  yield tracer the Pu-fraction is directly purified on a BIO-RAD AG® 1-X2 anion exchange column. The eluted fraction of Pu is evaporated, electrolysed and counted via low-level  $\alpha$ -spectrometry. With this method a detection limit of  $< 3$  mBq/kg is obtained for 30g soil aliquots in a three days count interval. This value is sufficiently low enough to meet typical environmental levels of even  $^{238}\text{Pu}$  in top-soil layers in Central Europe. Analyses of about 50 soil samples yielded typical  $^{239+240}\text{Pu}$  activity concentrations of about 0.5 Bq/kg and fairly constant  $^{241}\text{Am}/^{239+240}\text{Pu}$  and  $^{238}\text{Pu}/^{239+240}\text{Pu}$  activity ratios of  $0.36 \pm 0.03$  and  $0.03 \pm 0.01$ , respectively. The value obtained for  $^{241}\text{Am}/^{239+240}\text{Pu}$  can be well explained by production of  $^{241}\text{Am}$  from decay of pure  $\beta$ -emitting, short-lived  $^{241}\text{Pu}$  ( $T_{1/2} = 14$  years) taking the average initial atmospheric  $^{241}\text{Pu}/^{239+240}\text{Pu}$  ratio of about 13 at the peak of the nuclear weapon testing period about 40 years ago. With additional measurements of  $^{90}\text{Sr}$ ,  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  rough estimates were performed to calculate the relative contributions of  $\alpha$ -emitting hot particles,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  resulting from the Chernobyl reactor accident on the total inventory of these isotopes measured in top soil layers from Central Europe. While Pu, Am and Sr from the Chernobyl source turned out to be insignificant with respect to the atomic bomb derived component, more than 80% of surface bound  $^{137}\text{Cs}$  in Swiss soil was deposited from fallout of fine grained aerosols that were released into the atmosphere during the Chernobyl supergau 15 years ago.

## INTRODUCTION

Monitoring of nuclear weapon testing fallout or accidental released neutron fission or activation products around nuclear facilities is of major concern for environmental immission investigations. Of particular interest are activity determinations of highly toxic radioisotopes such as  $^{90}\text{Sr}/^{90}\text{Y}$  and  $^{239,240}\text{Pu}$  due to their long residence time in the biosphere and bio-availability for certain dietary products. In order to obtain the levels of the present-day radionuclide inventory in the immediate and near-by vicinity around the Swiss facility for surface storage of radwaste from all national nuclear power plants prior to the operational phase, an analytical program was started to determine the most relevant cosmic, terrestrial and anthropogenic radioisotopes in environmental samples. Of particular interest was the development of fast procedures for analysis of pure  $\alpha$ - and  $\beta$ -emitting radioisotopes in order to guarantee rapid throughput of several samples if there is any evidence for environmental radionuclide contamination following accidental release. In the course of this investigation, over 50 soil samples were analysed for terrestrial ( $^{40}\text{K}$ , U- and Th-series), cosmic ( $^7\text{Be}$ ,  $^{14}\text{C}$  (the latter

on tree leaves)), and anthropogenic isotopes ( $^{90}\text{Sr}$ ,  $^{134}\text{C}$ ,  $^{137}\text{Cs}$ ,  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ ). The analytical techniques applied and isotope relationships between these radionuclides are discussed in the following.

## METHODS

### Separation Procedure for $^{239+240}\text{Pu}$ and $^{241}\text{Pu}$

The principle of the Pu isolation from the chemical matrix is based on anion exchange chromatography and subsequent  $\alpha$ -spectrometry. If pure  $\beta$ -emitting  $^{241}\text{Pu}$  is to be determined an aliquot of the purified Pu-fraction can be taken for counting via  $\alpha/\beta$ -LSC. The method is as follows: 25ml 65%  $\text{HNO}_3$  and about 10 mBq of a  $^{242}\text{Pu}$  tracer solution (for samples with  $^{239}\text{Pu}$  concentrations of about 1 Bq/kg) are distributed homogeneously to a 30 g soil sample aliquot weighted in a 200 ml glass beaker. The beaker is then covered with a watch glass and the wet slurry is heated gently. As soon as the development of nitric gases has been ceased (ca. 30 minutes), the sample is taken to dryness and is then dry-ashed in an oven for 30 minutes at  $400^\circ\text{C}$ . After cooling to ambient temperature, the ash is stirred-up with 100 ml 8 M  $\text{HNO}_3$  and 2 ml 30%  $\text{H}_2\text{O}_2$  and then leached for 1 hour under boiling. The aqueous solution is then separated from the leached residue via filtration and the solid phase is washed twice with 30 ml  $\text{HNO}_3$  8 M. The liquid phase (in total about 150ml) is directly passed through an anion exchanger (BIO-RAD AG 1-X2, 100-200 mesh, column height in water 45 mm, diameter 10 mm) and potentially interfering isotopes from the U- and Th-decay series are eluted sequentially using additions of each 20 ml 8 M  $\text{HNO}_3$  and 10 M  $\text{HCl}$  washing solutions. The purified Pu-fraction is then eluted into a glass beaker containing 2ml  $\text{H}_2\text{O}$ , 1 ml 98%  $\text{H}_2\text{SO}_4$  and 0.1 ml 1 M  $\text{NaHSO}_4$  solution. The elution is carried out by rinsing the column with 20 ml of a solution consisting of 9 M  $\text{HCl}$  + 0.1 M  $\text{HI}$  (the latter causes reduction to Pu(III)). After evaporation to dryness the residue is dissolved in 2 ml  $\text{H}_2\text{O}$ . While 1 ml is taken for source preparation (via electrolysis in acid medium consisting of 0.6 ml 1 M  $\text{NaHSO}_4$  and 9 ml 0.5 M  $\text{Na}_2\text{SO}_4$  solution, details in Bajo and Eikenberg, 1999) and subsequent  $\alpha$ -spectrometry (model Octette, EG&G Ortec) the other 1 ml aliquot is transferred in a 20 ml 2/1 cocktail mixture consisting of Packard Ultima Gold™ A/B + F (for optimising  $\alpha/\beta$  pulse shape as well as peak energy resolution). This fraction is counted on Packard  $\alpha/\beta$ -LS-spectrometer model TriCarb® 2770SL/BGO equipped with a BGO detector guard for further background suppression using coincidence/anticoincidence electronics.

### Separation Procedure for $^{89}\text{Sr}$ and $^{90}\text{Sr}$

The method for separation of radioactive Sr-isotopes from soils is similar to procedures based on extraction chromatography on SrSpec™ resin (EiChrom Technologies), which was initially introduced by Vajda et al. (1992) and which is still among the most efficient rapid methods for determination of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in environmental materials at present days. At PSI a slightly modified method is used which reduces the effort for chemical yield determination simply by counting added  $^{85}\text{Sr}$  besides  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in a second  $\beta$ -window or via ICP-measurement of stable Sr before and after the extraction chromatographic step. This eliminates the need for a second precipitation step following the extraction for gravimetric yield determination. Ashing and leaching is identical to the method for determination of Pu but this time by adding a few Bq of a  $^{85}\text{Sr}$ -tracer. Prior to the extraction, a preceding precipitation step is carried out using oxalic acid at pH 5-6. This step is required because the distribution coefficient for Sr on SrSpec™ resin decreases significantly in presence of large quantities of alkaline elements (particularly

potassium). The oxalate precipitate is dissolved under boiling in 20 ml 65% HNO<sub>3</sub> until the oxalic acid has been destroyed completely (clear colourless solution). This solution is taken to dryness again, is re-dissolved in 15 ml 3 M HNO<sub>3</sub> and passed through a commercially available SrSpec™ column (EiChrom, Darien, IL). After passing through of the sample solution, the column is rinsed four times with 3 M HNO<sub>3</sub>. For routine analysis (i.e. environmental monitoring of <sup>90</sup>Sr) the Sr-fraction is then directly eluted with 10 ml 0.05 M HNO<sub>3</sub> into a 20 ml LS-vial and mixed with 10 ml of a scintillation liquid that is characterized by a high water loading capacity such as Ultima Gold™ LLT. If <sup>89</sup>Sr is of concern besides <sup>90</sup>Sr (for instance after accidental release) it is recommended to allow <sup>90</sup>Y to build up onto the column (1-2 days) and to analyse two cocktails (one with a pure <sup>90</sup>Y fraction counted in Cherenkov mode and the other mixed with scintillation cocktail for precise <sup>89,90</sup>Sr counting).

## RESULTS AND DISCUSSION

### Environmental levels of <sup>239,240</sup>Pu and <sup>241</sup>Pu

In Switzerland present day environmental levels of <sup>239+240</sup>Pu in topsoil layers vary between 0.1 and a few Bq/kg depending on the soil type and altitude (Geering et al., 2000). Contribution of atmospheric fallout Pu is higher in the Alps while the flat valleys in northern Switzerland are less affected. Soils from forest ecosystems show also higher levels over cultivated areas because of the higher filtration effect of forests for aerosol deposition on leaves compared to farmland with a less specific surface area of plants. In the vicinity of PSI the <sup>239+240</sup>Pu-values (circles in figure 1) scatter typically between 0.2 and 0.8 Bq/kg with an average of 0.5 Bq/kg. The data presented in figure 1 were obtained via high-resolution  $\alpha$ -spectrometry i.e. a counting technique, which enables to furthermore determine very low levels of <sup>238</sup>Pu. This isotope was released into the atmosphere by ignition and disintegration of the satellite SNAP-9A in 1964. Contribution of <sup>238</sup>Pu on total Pu is, however, insignificant in the soil samples analyzed here and elsewhere in Switzerland (Geering et al., 2000) and the <sup>238</sup>Pu/<sup>239+240</sup>Pu ratio of  $0.03 \pm 0.01$  calculated via regression analysis agrees well with that obtained from other sites in the northern hemisphere (Hoelgye et Filgas, 1995, Hodge et al., 1996). Figure 1 shows also the <sup>241</sup>Am vs. <sup>239+240</sup>Pu data of the same samples, which show strong correlation and the regression line through the data yields a result for <sup>241</sup>Am/<sup>239+240</sup>Pu of  $0.38 \pm 0.04$ . This result is within uncertainty identical to the present day <sup>241</sup>Am/<sup>239+240</sup>Pu ratio of 0.36 calculated via <sup>241</sup>Pu/<sup>241</sup>Am progenitor/progeny relationship (figure 2) and additionally considering that the initial <sup>241</sup>Pu/<sup>239+240</sup>Pu ratio resulting from nuclear weapon testing in the 60ies was about 13 (UNSCAER, 2000). This result shows clearly that <sup>241</sup>Am measured in the samples analysed here can be well explained via support from decaying <sup>241</sup>Pu initially released during the surface A-bomb testing period meaning that contribution of heavy particles from the Chernobyl accident are not significant in Central Europe.

### Calculation of the fraction of radioactive fallout products from various sources

Disregarding significant contribution of actinides from the Chernobyl accident to the inventory of Pu in Central Europe, and inserting the average <sup>239+240</sup>Pu/<sup>137</sup>Cs ratio reported for North American soils (i.e. pure atomic bomb component) as the initial pre-Chernobyl Pu/Cs ratio, then the fractions of <sup>137</sup>Cs from both events can be roughly estimated (all equations in Table 1). A more precise result for both components is, however, obtained via the measured <sup>134</sup>Cs/<sup>137</sup>Cs ratio. This is of advantage, because both isotopes are from the same element, i.e. behave chemically

identical, while Pu and Cs do not have the same transport and transfer properties. The following approach is made here: since  $^{134}\text{Cs}$  is a short-lived radionuclide ( $T_{1/2} = 2.6$  years) the fraction of this isotope

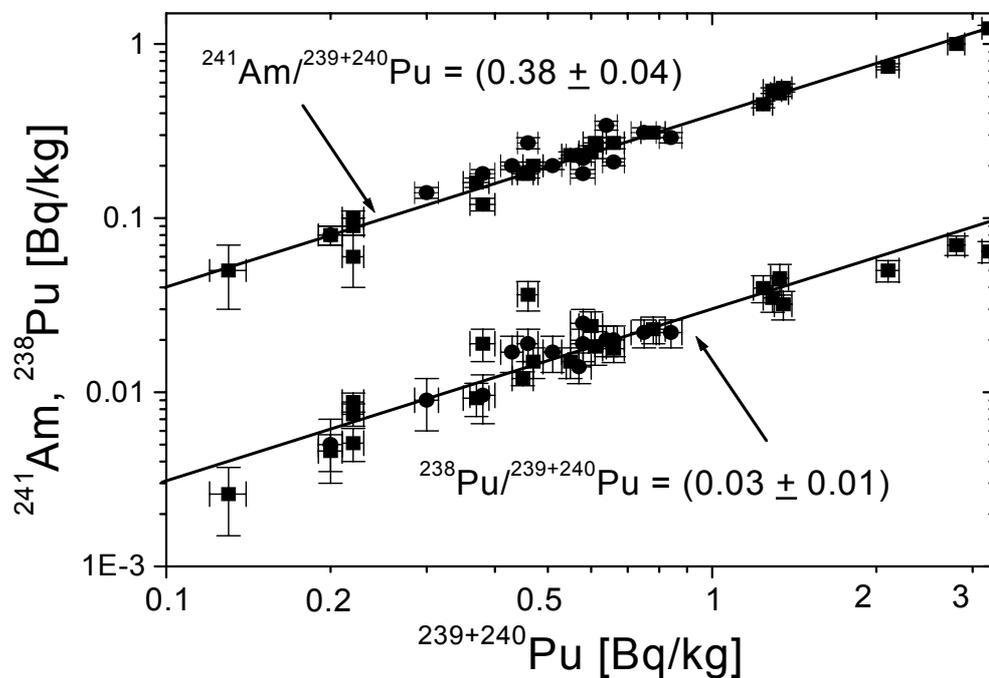


Figure 1: Correlation diagram with  $^{238}\text{Pu}$  vs.  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ , vs.  $^{239+240}\text{Pu}$  obtained on Swiss soil samples from various locations (circles = data from this work, squares = data from Gering et al., 2000).

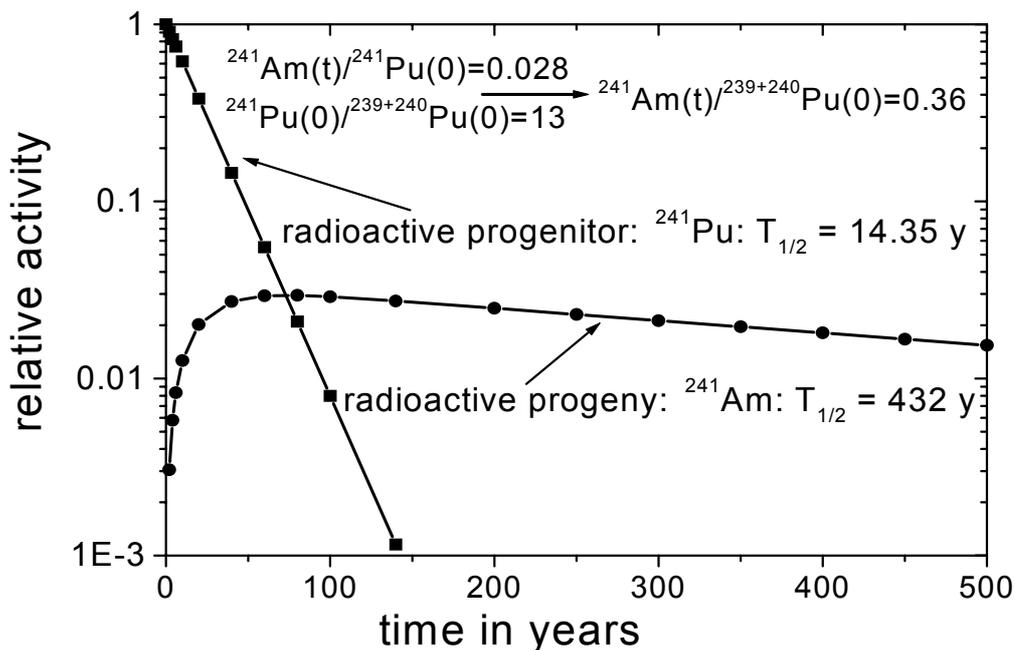


Figure 2: Progeny/progenitor relationship for the  $^{241}\text{Pu}/^{241}\text{Am}$  couple with time.

from the surface bomb testing period of the 60ies has been decayed completely, meaning that measured  $^{134}\text{Cs}$  is derived from the Chernobyl accident solely. Inserting, in addition, the initial  $^{134}\text{Cs}/^{137}\text{Cs}$  ratio for aerosols in the Chernobyl plume after explosion, it is possible to precisely calculate the contribution of  $^{137}\text{Cs}$  from both nuclear sources at any time as long as  $^{134}\text{Cs}$  can be monitored. As shown in Table 1 both approaches yield similar results and indicate that more than 80% of surface bound  $^{137}\text{Cs}$  in Central Europe can be attributed to fallout of very fine aerosols from the Chernobyl supergau in 1986. A similar consideration can be made with respect to  $^{90}\text{Sr}$  by use of the measured (as well as reported initial)  $^{90}\text{Sr}/^{137}\text{Cs}$  ratio and the fractional distribution of  $^{137}\text{Cs}$  in both nuclear components (as derived from  $^{134}\text{Cs}/^{137}\text{Cs}$ ). However, in contrast to  $^{137}\text{Cs}$  the calculation yields in this case that the amount of  $^{90}\text{Sr}$  from the bomb tests exceeds by far that resulting from the Chernobyl source, indicating that released  $^{90}\text{Sr}$  was fixed on more coarse grained particles with significantly lower residence time in the atmosphere.

**Table 1.** Calculated fractions of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in Swiss soil samples that were contaminated by fallout products from previous (40-year-ago) atmospheric nuclear bomb testing (component B) and from the 1986 Chernobyl accident (component C) (reference date: October 6, 1997).

	end component activity ratio ( $R_B$ or $R_C$ )	measured activity ratio ( $R_m$ )	bomb to Chernobyl fallout ratio ( $R_{Cs}$ and $R_{Sr}$ )
1	$R_B = \left( \frac{^{239+240}\text{Pu}}{^{137}\text{Cs}} \right)_B = 3 \cdot 10^{-2} (1)$	$R_m = \frac{^{239+240}\text{Pu}_B}{^{137}\text{Cs}_B + ^{137}\text{Cs}_C} = 4.8 \cdot 10^{-3}$	$R_{Cs} = \frac{^{137}\text{Cs}_B}{^{137}\text{Cs}_C} = \frac{R_m}{R_B - R_m} = 0.18$
2	$R_C = \left( \frac{^{134}\text{Cs}}{^{137}\text{Cs}} \right)_C = 1.6 \cdot 10^{-2} (2)$	$R_m = \frac{^{134}\text{Cs}_C}{^{137}\text{Cs}_B + ^{137}\text{Cs}_C} = 1.4 \cdot 10^{-2}$	$R_{Cs} = \frac{^{137}\text{Cs}_B}{^{137}\text{Cs}_C} = \frac{R_C - R_m}{R_m} = 0.15$

3	$R_B = \left( \frac{{}^{90}\text{Sr}}{{}^{137}\text{Cs}} \right)_B = 6 \cdot 10^{-1} (3)$	$R_m = \frac{{}^{90}\text{Sr}_B + {}^{90}\text{Sr}_C}{{}^{137}\text{Cs}_B + {}^{137}\text{Cs}_C} = 7.4 \cdot 10^{-2}$	$R_{Sr} = \frac{{}^{90}\text{Sr}_B}{{}^{90}\text{Sr}_C} = \frac{R_B}{7.7 \cdot R_m - R_B} > 20$
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(1) from Hodge et al. (1996), (2) from NEA-OECD (1996), (3) from UNSCAER (2000) all values at reference date

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